SELENIUM

BY J. D. SARGENT

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INTRODUCTION

Selenium might be described as a paradoxical element, being a metal or a nonmetal, a conductor or nonconductor, amorphous or crystalline, colorant or decolorant, and a hydrogenator or dehydrogenator.

Selenium was discovered in 1817 by the Swedish chemist, Berzelius, while studying flue dust from the lead chambers of the sulfuric acid works at Gripsholm, Sweden.

The ordinary stable form of selenium is a crystalline, grayish solid with semimetallic luster. It melts at 220.2° C., boils at 684.8° C., and has a specific gravity of 4.47.

Selenium is closely related to sulfur, with which it is commonly associated in nature. It is found native, like sulfur, and also in the selenides of copper, silver, lead, mercury, bismuth, and thallium. About 25 minerals contain selenium in varying percentages, but none of the species is considered a commercial source. (See Appendix A)

The only commercial source of selenium at present is the anode mud or slime produced in the electrolytic refining of blister copper. The selenium content of blister copper anodes handled by domestic refineries ranges from 0.03 to 0.14 percent; the slimes generally contain 4 to 25 percent selenium.

Commercial uses for selenium began to develop on a substantial scale during the interwar period in the glass, ceramic, chemical, pigment, and rubber industries, and later in the stainless steel industry. Selenium rectifiers for converting alternating current to direct current were used industrially for many years but only on a small scale. In 1947 the miniature-type selenium rectifier for electronic circuits was developed. These diminutive rectifiers, as employed in voltage multiplier circuits for radio and television sets, eliminate heavy and bulky transformers and rectifier tubes. Military uses of the selenium rectifier cover a wide range.

Selenium is used in the glass industry as a decolorizer and in the stainless steel industry as an additive to improve machinability and to control the quality of castings. A diversified group of chemical uses, including pigments and rubber accelerators, now consumes more selenium than both the glass industry and the steel industry.

Domestic production of primary selenium from 1947 to 1951 averaged 514,988 pounds annually and was produced by 3 companies: American Smelting & Refining Co., U. S. Metals Refining Co. (subsidiary of American Metal Co., Ltd.), and International Smelting & Refining Co. Primary selenium production in the United States was

687,384 pounds in 1952 and 923,887 pounds in 1953, produced by the aforementioned companies and Kennecott Copper Corp. (see Appendix E). Demand existed for larger quantities of selenium than were available.

PHYSICAL AND CHEMICAL PROPERTIES

Selenium chemically resembles sulfur and like sulfur has several allotropic forms. Many of the allotropic forms can be grouped together and called reddish-brown selenium precipitates. The lightest of the reddish-brown allotropics has a specific gravity of 4.3 and softens at 60° C. Another of the reddish-brown allotropics is colloidal and fluoresces in water. Vitreous selenium is purple-black and can be formed by cooling the reddish-brown allotropics quickly. Slow heating the vitreous form to 65° C. or over will convert selenium to its most common form, silvery-gray metallic selenium. Hexagonal acicular crystals of metallic selenium are sometimes hollow and flexible, with a Moh's hardness of 2 and a melting point of 220.2° C. Selenium boils at 684.8° C., giving off dark-red vapors, and at higher temperatures will sublime, emitting yellowish vapors. Optically, metallic selenium is pleochroic and anisotropic with an "O" index of 3.0 and an "E" index of 4.04. Electrically, selenium is a photoelectric semiconductor. (See Appendix B for selenium atomic data.)

The chemical nature of selenium is apparent in the chemical usage of selenium and selenium compounds outlined under Usage in this circular.

GEOLOGY AND MINERALOGY

The selenium content of igneous rocks is about 0.09 p.p.m. Cores of marine sediments from the Continental Shelf average 1 to 2 p.p.m. selenium, whereas deep sea cores assay much lower (53).[2] Selenium assays of the Continental Shelf deposits correspond closely with the selenium content of the Sedimentary rock strata of Western United States and the soils derived from them (172).

A large area of North America - from Canada to Mexico and from the Mississippi to the Rocky Mountains - is underlain by seleniferous rocks and soils. Most of the seleniferous rocks are sedimentary formations ranging in age from the late Paleozoic era to the present. Rocks formed during the Cretaceus period have been found to be the most highly seleniferous. Limonitic concretions from the Cretaceous Niobrara formation contain from 20 to over 500 p.p.m., whereas the surrounding shales contain only 2 p.p.m. Phosphate rock from the Permian Phosphoria formation of western Wyoming was found to vary from 1 to 600 p.p.m. For a list of seleniferous formations, see Appendix C.

Soils derived from seleniferous rocks usually contain 2 or 3 p.p.m. selenium. Annual rainfall in the seleniferous area is not sufficient to leach even the more soluble compounds of selenium from the soil. Soils containing only 1 or 2 p.p.m. selenium commonly sustain plants with a selenium content of 50 to 10,000 p.p.m. and in one instance a record 14,920 p.p.m. Some plants are indicative of seleniferous soils. For a list of selenium indicator plants and their distribution, see Appendix D.

Aside from the selenium minerals themselves, magmatic sulfide deposits represent the greatest known concentration of selenium in the earth's crust. Average selenium content of magmatic sulfides is about 0.02 percent. A list of selenium minerals appears in Appendix A.

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[2] Underlined numbers in parantheses refer to items in the bibliography at the end of this report.

GEOGRAPHIC DISTRIBUTION AND FOREIGN PRODUCTION

Central and South America

Chile ranks second only to the United States as a copper producer but apparently produces no selenium or commercial products from which selenium is recovered in substantial amounts. Many occurrences of selenium minerals are reported from Argentian, Bolivia, Chile, and Honduras. None of these occurrences are known to be very extensive.

Africa

Northern Rhodesia and the Belgian Congo are also major producers of copper. Copper anodes from Rhodesian copper refineries assay 0.0141 percent selenium, and their slimes assay 12.64 percent selenium. Northern Rhodesia produced almost 30,000 pounds of selenium in 1952. Much of this selenium is recovered in Belgium and reported as Belgian production.

Australia

Selenium is produced in Australia by the Electrolytic Refining & Smelting Co. of Australia Pty., Ltd., Port Kembla, from the company's own anode muds and from those obtained from the Mount Lyell Mining & Railway Co., Queenstown, Tasmania. Australian production of selenium is about 4,000 pounds a year from slimes containing only 1 or 2 percent selenium. Mount Morgan, Queensland, blister copper contains 0.019 percent selenium, but no recovery has been recorded.

Asia

Selenium is recovered at the following Japanese copper refineries: Furukawa Electric Co., Ltd., Nikko, Tochigi Prefecture; Nippon Mining Co., Ltd., Hitachi, Ibaragi Prefecture; Mitsubishi Metal Mining Co., Ltd., Osaka, Osaka Prefecture; Mitsui Mining and Smelting Co., Ltd., Takehara, Hiroshima Prefecture; Sumitomo Metal Mining Co., Ltd., Niihama, Ehime Prefecture; Nippon Mining Co., Ltd., Saganoseki, Oita Prefecture and from the following sulfuric acid plants: Ishihara Mining Co., Ltd., Yokkaichi, Mie Prefecture; and Koatsu Mining Co., Ltd., Omuta, Fukuoka Prefecture. In addition, the Republic Chemical Corporation of Tokyo initiated selenium recovery in September 1952. Japan produces about 50,000 pounds of selenium annually.

U. S. S. R.[3]

Soviet Union selenium statistics have not been available since 1940. A review of what little information was available before that time is presented here:

During 1926-27 the U. S. S. R. consumed about 2,000 pounds of selenium a year, only one-third of which was produced in that country. U. S. S. R. annual selenium production potential during this period was estimated to be 6,000 pounds.

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[3] Based on information contained in Bureau of Mines files and from an unpublished manuscript by Alexander Gakner of Falls Church, Va.

Russia produced 5,000 pounds of selenium in 1931 from electrolytic slimes and was preparing to recover selenium from sulfuric acid production byproducts in 1932.

Selenium content of 7 percent has been recovered from the Kyshtym electrolytic slimes since 1928, and recovery exceeded 2,000 pounds per year by 1934. A Moscow electrolytic plant, with a potential production of 4,000 pounds of selenium per year from 4-percent selenium slimes, was completed in 1935. Selenium has also been recovered from Cottrell-precipitator dusts at a super-phosphate plant in Odessa since 1935. Another reference to these same dusts, however, stated that the by-product recovered was tellurium.

Selenium recovery from the Belovo zinc-lead ores of the Altai region was initiated about 1938.

The United States imported 2,762 pounds of selenium from the U. S. S. R. in 1939 and 11,056 pounds in 1940. No selenium has been imported from the U. S. S. R. since 1940.

Judging from U. S. S. R. copper production in 1953, Soviet selenium production would be about 100,000 pounds per year.

Several seleniferous ores are known to occur in the U. S. S. R. The Karabash, Kalata, and Krasnouralsk copper and pyrite deposits in the Ural Mountains contain as much as 0.025 percent Se. Ores from Obnovlennyy Rudnik contain 0.14 to 0.24 percent selenium. The Kedabek pyrite deposit in the Caucasus assays 0.0143 percent. The Medredevka barite deposits in the Ural Mountains are reported to be seleniferous.

Europe

Sweden is generally the largest European producer, and during 1951 Swedish slenium output was 90,000 pounds. Most of this production can be attributed to Boliden Gruv AB, operating several mining properties in the Skelleftea region and a smelter and electrolytic refinery at Skellefthawn.

Several Norwegian firms planned to initiate selenium recovery in 1953, and the Outokumpy Oy in Finland produces a small quantity of selenium.

Belgium is a significant selenium producer and exported more than 22,000 pounds in 1951, more than 37,000 pounds valued at $616,240 to 17 foreign countries in 1952, and more than 61,000 pounds valued at $957,080 to 15 foreign countries in 1953. Metallurgie de Hoboken, the major Belgian producer, obtains most of its selenium-bearing ores from Africa.

Western Germany produced over 16,000 pounds of selenium in 1951; the Norddeutsche Affinerie of Hamburg is the major producer. Much of its selenium raw material is imported from South America.

International Nickel Co. of Canada upgrades selenium at its Clydach refinery near Swansea, Wales, United Kingdom. Production from this plant is included in Canadian statistics.

In southeastern Yougoslavia, the Bor Copper Mining Corp. electrolytic refinery recovers about 1,000 pounds of selenium per year.

In Linate, near Milan, Italy, the Montecatini group recovers selenium from copper sulfate.

North America

Mexico is a major selenium producer, but most of their selenium is recovered and refined in the United States and is included in the United States production statistics.

Selenium is produced in Canada by the International Nickel Co. at Copper Cliff, Ontario, and by Canadian Copper Refiners, Ltd., Montreal East, Quebec. The latter plant, which treats blister copper produced by Noranda Mines, Ltd., and by Hudson Bay Mining & Smelting Co. has a rated annual production capacity of 450,000 pounds of selenium, but its 1950 output was less than 350,000 pounds, after declining gradually from its peak output of 521,867 pounds in 1946 (147, 148). This decline reflects the reduction in output of selenium-rich, high-grade ores from the Horne Mines at Noranda and a larger proportion of copper obtained from other mines. The Hudson Bay blister is usually high in selenium, available analyses showing 0.18 percent of this element. The efficiency of selenium recovery at this plant is extraordinarily high. The International Nickel Co. gets most of its selenium-bearing ore from the Sudbury Basin in Ontario, which has an ore reserve containing an estimated 3,000,000 pounds of selenium. The Copper Cliff refinery has a 270,000-pound capacity for selenium production.

The United States is the world's leading producer of selenium.

DOMESTIC PRODUCTION, CONSUMPTION, AND FOREIGN TRADE

The American Smelting & Refining Co. (Baltimore, Md.), United States Metals Refining Co. (Carteret, N. J.), International Smelting & Refining Co. (Perth Amboy, N. J.), and Kennecott Copper Corp. (Garfield, Utah) are the principal selenium producers in the United States. In addition, several companies such as Kawecki Chemical Co., Boyertown, Pa.; and Vickers Electric Division, Vickers, Inc., St. Louis, Mo., recover selenium from scrap of rectifier manufacturers and spent catalysts and also upgrade commercial-grade selenium into high-purity selenium. In 1953 the Kawecki Chemical Co. initiated selenium recovery from sulfuric acid-production by-products.

Domestic production of selenium from 1947 to 1951 averaged 514,988 pounds annually. Total 1952 primary selenium production was 687,384 pounds and 66,781 pounds of secondary selenium were recovered. A total domestic primary selenium production of 923,887 pounds and 97,948 pounds of secondary production was attained in 1953. A goal of 1,100,000 pounds of domestic selenium production was set for 1955.

Apparent domestic consumption (producers' domestic shipments plus imports to consumers) of selenium has ranged during the 5 years from about 600,000 to over 1,000,000 pounds, averaging 848,460 pounds annually. Producers' domestic shipments in the period averaged 536,215 pounds and imports to consumers 312,245 pounds. The trend since this period has been toward greater domestic shipments and lesser consumer imports. Apparent domestic consumption of selenium in 1952 was 802,033 pounds and 1,189,930 pounds in 1953. Demand in the 1951-52 period for selenium and selenium compounds exceeded 1,500,000 pounds and was steadily increasing, with no hope of fulfillment in the foreseeable future.

Exports of selenium by producers were at a low level during the 1947-51 period, averaging 27,321 pounds annually. Exports since this period have been at an even lower level and under strict Government control.

Imports of selenium from 1947 to 1951 averaged 315,568 pounds per year. A record 529,175 pounds of selenium was imported in 1947, largely from Canada. Total selenium imports in 1952 were only 123,135 pounds, and 99,865 pounds in 1953. This included imports from Canada under toll arrangement.

The National Production Authority placed both imported and domestically produced selenium under complete allocation in February 1952, explaining that the action was necessary if essential defense requirements were to be met. Allocation was terminated in early 1953, but the shortage continues.

The outlook is not favorable under a continuation of existing circumstances for obtaining increased supplies of selenium from the usual sources, to meet expanding requirements, or to provide for full mobilization needs.

METALLURGY

Blister copper averages about 0.05 percent selenium. About 25 percent of the selenium content of copper ores has been lost before the blister copper stage is reached. Blister copper is converted to refined copper by electrolysis. Anode muds or slimes are a byproduct of this electrolytic refining. Anode slimes contain from 4 to 25 percent selenium, averaging about 8 or 9 percent. The recovery of selenium from anode slime is different at each individual plant.

Tyler's selenium report (173) summarizes several selenium recovery processes that have been used as follows:

(a) Oxidizing roast: Shallow layers of slimes are heated to 500 to 800 degrees F. with plenty of air. Some selenium and arsenic are volatilized. The calcine is leached with H_2SO_4, foul electrolyte, or liberator solution, and the solution sent to the electrolytic department. Selenium is precipitated as copper selenide in the liberator system but is easily recovered.

(b) Sulphating roast: Concentrated sulphuric acid is added to the slimes prior to charging, or during the roast, by spraying. Selenium and tellurium are oxidized to the corresponding oxides or oxysulphates. Roasting at high temperature drives off selenium dioxide, but too high temperatures (over about 1200 degrees F.) tend to decompose copper sulphate. Roasted slimes are leached with hot water. The leach liquor contains silver and some selenium and tellurium, all of which are precipitated by cementation with metallic copper or raw slimes. Selenium requires a somewhat longer cementation time than silver, and tellurium is even more resistant to cementation than selenium.

(c) Boiling with dilute H_2SO_4 and niter: This process is of only historical interest due to high chemical cost, fume disposal problems, impure solutions, excessive corrosion of equipment, and other disadvantages.

(d) Aeration in dilute H_2SO_4: A suspension of slimes in hot dilute H_2SO_4 is blown with air. This dissolves metallic copper and leaves selenium and tellurium in the slimes, along with gold and silver. This process is economical of acid, but this is partially offset by the cost of steam. Equipment is simple, but bulky, and corrosion problems are not serious.

(e) Pyrometallurgical methods: Direct smelting of slimes has been virtually abandoned, as have various attempts to treat selenide matte in small converters or tank furnaces. The sodium bisulphate process recently adopted by Kennecott, however, is in this category. Soda smelting is a pyrometallurgical method, but in commercial practice the raw slimes are first decopperized by acid leaching or some other method.

(f) Miscellaneous methods: A number of methods have been proposed for treating raw slimes, including aeration in aqueous solutions of ammonia, etc., aeration in aqueous cyanides, chlorination, and treatment with manganese dioxide and H_2SO_4. None of these methods, however, have proven commercially feasible.

The sulfate roast process is used by the Canadian Copper Refiners, Ltd., of Montreal East, Quebec.

The American Smelting & Refining Co. utilized the soda-smelt process for many years at Baltimore. The nature of recent process changes at this plant has not been disclosed.

Kennecott Copper Co. fused selenium slimes with sodium bisulfate after first leaching out copper with acid.

The Perth Amboy, N. J., plant of the International Smelting & Refining Co. converted slimes to alkaline slags. The selenium content of these slags was dissolved with sulfuric acid and then acidified with hydrochloric acid. Elemental selenium was then precipitated with sulfur dioxide.

At the Copper Cliff, Ontario, refinery, International Nickel Co., the slimes, were first fluxed with sand and fluorspar. The resulting matte was refined to dore and the soda niter slags were leached with water. Selenium was recovered from this leach water by precipitation as "coke" selenium.

In some plants, slimes and fume products from other metal-refining operations are added to the byproducts recovery processes along with selenium scrap and spent selenium catalysts. In addition, many fractions are recycled and reprocessed, the net result being a rather complicated operation. Since these raw materials are seldom assayed, the source of any given batch of selenium is unknown.

Slime treatment processes are primarily designed to recover the precious metals. Selenium and tellurium recovery are of secondary importance. Frequent changes are made in slime treatment processes to increase recovery rates, lower costs, and accommodate changes of raw materials.

The selenium end product of all of these processes is commercial-grade selenium (97.2 to 99.94 percent pure) usually in coke form. This coke selenium is pulverized and sold as commercial-grade selenium or further refined to high-purity selenium (99.99+ percent). Ferroselenium is produced as a byproduct of high-purity selenium production. Ferroselenium can be used directly in the production of stainless steel.

In 1953 selenium-production facilities were sufficient for much larger operations had an increased supply of slimes become available.

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USAGE (149, 178)

Before World War I, selenium was regarded as the abomination of the smelterman and was discarded. Even with the present strong demand, selenium is regarded of minor importance as compared with precious-metal byproducts. During that war, when manganese was in short supply, selenium first came into use as a substitute to decolorize glass by neutralizing the greenish tinge imparted by iron impurities. Inasmuch as selenium has certain inherent advantages over manganese in the decolorization of glass, its use continued after manganese again became available.

The glass industry continued to be the major consumer of selenium until after World War II, when the selenium-rectifier industry became the principal consumer. Selenium rectifiers have been known since 1884 but were not used extensively until about 1930, when German and American investigators improved the device. Selenium dry-plate rectifiers change alternating to direct current and are extensively used in electroplating, welding, direct current motor operation, battery chargers, magnet coils, and arc lamps. Additional military uses of selenium rectifiers include aircraft controls, degaussing equipment, dynamotor power, guided missiles, ground starters for aircraft, magnetic amplifiers, radar equipment, relay and solenoid power, sonar equipment, telephones, teletypes, and voltage regulators. The largest increase in rectifier use occurred in 1947, when minature rectifiers suitable for radio and television circuits were developed. These diminutive rectifiers, used in voltage multiplier circuits of radio or television sets, can deliver 200 to 500 volts d.c. from a 117-volt a.c. source, eliminating a heavy and bulky transformer and rectifier tube and saving more than 1/2 pound copper and 7-1/2 pounds of steel per television set. (See fig. 1.)

Selenium has photoelectric conductivity, as well as rectification properties. Selenium photoelectric cells are used in photographic exposure meters, electric eyes, colorimeters, and pyrometers.

As previously noted, selenium is added to glass to alter the greenish tinge of iron impurities to a neutral gray. From 0.1 to 0.3 pound of metallic selenium, sodium selenite, barium selenite, or sodium selenate per ton of glass is required, the exact quantity being determined by the iron content to be neutralized. Excess selenium causes a pink tinge, which is desirable in the case of milk bottles and a few other food-containers. From 1 to 5 pounds of selenium per ton of glass yields a very desirable ruby-red glass, which is used in tableware, taillight-signal lenses, light filters, infrared equipment, lantern globes, and traffic lights.

Selenium is important in the rubber industry. Added mostly in the form of selenium diethyl dithiocarbamate, selenium acts as an accelerator and vulcanizing agent and, in addition, promotes resistance to heat, oxidation, and abrasion and increases the resilience of rubber.

Selenium as sulfoselenide is used as a pigment to product orange, red, and maroon colors in paint, soap, rubber, ceramics, paper, printing inks, plastics, dyes, leather, and other products.

Selenium and its compounds are widely employed in industrial and research chemistry. Selenium dioxide oxidizes organic compounds, producing reactions not obtainable by any other known method. Selenium can be either a hydrogenating or dehydrogenating agent. Occasionally, 10 times as much selenium as organic compound is required during dehydrogenation. Selenium is a hydrogenation and cracking catalyst in crude oil and coal distillations. Soaps, waxes, edible fats, and plastics are produced by fat hardening with a selenium catalyst. The Kjeldahl method

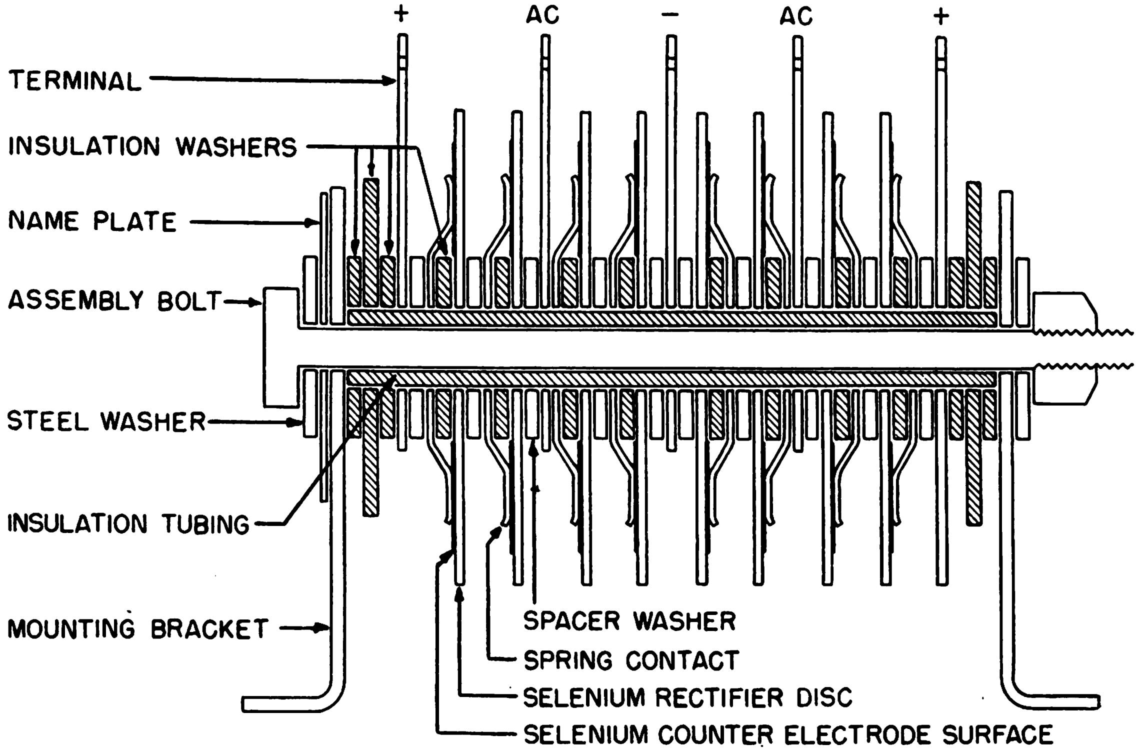

Figure 1. - Cut-away view of typical rectifier stack assembly.

of nitrogen determination utilizes a selenium catalyst. It imparts exceptional antioxidant properties to printing ink, mineral oils, transformer oils, and vegetable oils. Nondrying properties of linseed, oiticica, and tung oils are due to selenium. Selenium also retards gelation in tung oil. The antioxidant and antigalling properties of selenium compounds find application in lubricating oils and in extreme pressure lubricants. Selenium is the catalyst that synthesizes cortisone, used to treat arthritis, and isonicotinic acid, used to treat tuberculosis. Selenium compounds are found in dandruff, dermatitis, and deoderant pharmaceuticals. Selenium compounds are finding wide application as insecticides, fungicides, parasiticides, bacteriocides, and herbicides. Photographic photosensitizers and toning baths contain selenium compounds such as sodium selenosulfate. Blasting caps, mercury vapor detectors, flotation reagents, fireproofing agents, insect repellants, phosphorescents, and luminescents can be made from selenium compounds.

Care must be exercised in such widespread usage, inasmuch as selenium and most of its compounds are toxic or corrosive. Selenium oxychloride is so corrosive that it is known as the universal solvent.

Selenium improves the machinability of stainless steel. Forging steels contain 0.18 to 0.22 percent selenium and the full machining grade 0.30 to 0.35 percent. In cast steel 0.01 percent to 0.05 percent selenium assures a fine-grained, bubble-free casting. Small quantities of selenium improve machinability and tensile strength of copper and copper-rich alloys without appreciably lowering ductility or conductivity.

Xerography, a dry photographic process, employs selenium-coated metal disks from which the photographic image is transferred by static electricity.

Radioactive selenium has been utilized in radiography.

Percentagewise, the electrical industry and the chemical industry each consume about 40 percent of this Nation's selenium. The glass industry uses about 13 percent of the total available supply, and the steel industry consumes the remaining 7 percent.[4]

APPENDIX A

Selenium Minerals[5]

Native selenium - Se
Selen-tellurium - (Se, Te)
Selenian sulfur - (Se, S)
Aguilarite - $Ag_2(Se,S)$
Naumannite - Ag_2Se
Berzelianite - Cu_2Se
Crookesite - $(Cu,Tl,Ag)_2Se$
Eucairite - $CuAgSe$
Umangite - Cu_3Se_2
Clausthalite - $PbSe$
Tiemannite - $HgSe$

Klockmannite - $CuSe$
Guanajuatite - Bi_2Se_3
Penroseite - $(Ni,Cu,Pb)Se_2$
Wittite - $Pb_5Bi_6(S,Se)_{14}$
Weibullite - $PbBi_2(S,Se)_4$
Platynite - $PbBi_2(Se,S)_3$
Selenolite - SeO_2
Ahlfeldite - $Ni(SeO_4).6H_2O$
Chalcomenite - $CuSeO_3.2H_2O$
Cobaltomenite - $CoSeO_3.2H_2O$
Kersterite - $PbSeO_3.2H_2O$

Other minerals that occasionally contain isomorphic or interstitial selenium are native tellurium, melonite, lillianite, emmonsite, metacinnabar, chiviatite, and many sulfides and sulfosalts, especially those containing iron and copper.

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[4] Derived from statistics supplied by the Bureau of the Census.

[5] Only lists minerals accredited by Palache, Berman, and Frondel in Dana's system of Mineralogy, J. Wiley & Sons, Inc., 7th ed., 1944.

An unnamed Co-Ni-Cu selenide is described by Robinson and Brooker.[6]

APPENDIX B

Selenium

Chemistry and Physics[7]

Atomic number: 34 Period: IV Group: VI

Atomic weight: International atomic weight in 1925, 79.2; changed to 78.96 in 1949. Isotope abundance as follows:

Se^{74} - 0.87, Se^{76} - 9.02, Se^{77} - 7.58, Se^{78} - 23.52.

Se^{80} - 49.82, Se^{82} - 9.19.

Valence: 2, 4, or 6.

Electronic configuration: 34 electrons in 4 shells as follows:

K	L		M			N			
1	2		3			4			
S	S	P	S	P	D	S	P	D	F
2	2	6	2	6	10	2	4		

Radiation of isotopes: Artificially radioactive.

			Radiation energy (MEV)	
Isotope	Type of radiation	Half-life	Particles	Rays
Se^{70}	B^+	44 min.		
Se^{72}	K	9.5 days		
Se^{73}	B^+, K	6.7 to 7.1 hr.	1.29	
Se^{75}	K, gamma, e^-	115 to 127 days		0.77 to 0.5
Se^{77m}	I.T., gamma	17.5 sec.	.135e^-	.15
Se^{79m}	I.T., e^-	3.9 min.		.096
Se^{79}	B^-	6 x 10^4 yr.	.16	
Se^{81m}	I.T., e^-	57 to 59 min.		.099
Se^{81}	B^-	17 to 19 min.	1.5	
Se^{83m}	B^-, gamma	67 sec.	3.4	
Se^{83}	B^-, gamma	25 to 30 min.	1.5	.017 to 1.1
Se^{84}	B^-	2.5 min.		

Stable isotopes: Se^{74}, Se^{76}, Se^{77}, Se^{78}, Se^{80}, Se^{82}

U^{235} fission products: Se^{79}, Se^{81m}, Se^{81}, Se^{83m}, Se^{83}, Se^{84}

Polarizability of the free anion of selenium = 112 x 10^{25}

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[6] Robinson and Brooker: Am. Mineral, vol. 37, 1952, pp. 542-44.

[7] Sources include: Nuclear data, Circular of the National Bureau of Standards 499, September 1950; Handbook of Chemistry & Physics, 33d. ed.; and Stokley, James, Nuclides and Isotopes, General Electric, 1953.

APPENDIX C

Seleniferous Formations[8]

Tertiary

Fort Union formation, Tuscher formation, Wasatch formation, Wind River formation, Bridger formation, Uinta Mountain group, Duchesne River formation, Chadron formation, Arikaree group (formation), Browns Park formation, North Park formation.

Cretaceous

Cloverly formation, Gannett group, Thermopolis shale, Dakota sandstone (quartzite west of Front Range, sandstone east of Front Range, formation in Kansas and Minnesota, group in and to the northeast of the Front Range), Aspen shale, Mowry shale, Mancos shale, Frontier formation, Carlile shale, Niobrata formation, Hilliard formation, Steele shale, Iles formation, Williams Fork formation, Lewis shale, Pictured Cliffs sandstone, Fruitland formation, Kirtland shale, McDermott formation, Lance formation, Medicine Bow formation, Mesaverde formation.

Jurassic (?)

Bear River formation

Jurassic

Wingate sandstone, Kayenta formation, Curtis formation, Sundance formation, Summerville formation, Morrison formation, Gannett group.

Triassic

Dinwoody formation, Moenkopi formation, Chugwater formation, Chinle formation.

Permian

Supai formation, Cutler formation, Phosphoria formation, Chugwater formation.

Permian (?)

Rico formation.

Pennsylvanian

Amsden formation, Paradox member, Hermosa formation.

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[8] Modified from Trelease, S. F., and Beath, O. A. (172)

APPENDIX D

Selenium Indicator Plants[9]

(See fig. 2.)

Astragalus

Species	Distribution
Astragalus bisulcatus (Hook.) (Gray)	Alba., Sask., Man., Mont., N. Dak., Idaho, Wyo., S. Dak:, Nebr., Colo., Okla., Kans., N. Mex.
A. diholcos (Rydb.) (Tidestrom)	Wyo., Colo.
A. haydenianus (Gray)	Wyo., Utah, Colo., Nev., N. Mex.
A. oocalycis (Jones)	Colo., N. Mex.
A. racemosus (Pursh)	Alba., Mont., N. Dak., Wyo., S. Dak., Nebr., Utah, Colo., Kans., N. Mex. Okla., Tex.
A. osterhouti (Jones)	Colo.
A. albulus (Woot. & Stand)	Ariz., N. Mex.
A. argillosus (Jones)	Utah, Ariz.
A. confertiflorus (Gray).....................	Wyo., Utah, Colo., Ariz., N. Mex.
A. confertiflorus var. flaviflorus (Kuntze) (Jones)	Wyo., Utah, Colo.
A. moencoppensis (Jones)	Utah, Ariz.
A. grayi (Parry)	Wyo., Mont.
A. pectinatus (Dougl.)	Alba., Sask., Man., Mont., N. Dak., S. Dak., Utah, Wyo., Colo., Kans.
A. pectinatus var. platyphyllus (Jones)	Wyo.
A. toanus (Jones)	Idaho, Utah., Nev.
A. beathii (Porter)	Ariz.
A. eastwoodae (Jones)	Utah
A. ellisiae (Porter)	N. Mex.
A. crotalariae (Benth.) (Gray)	Calif., Nev., Ariz.
A. pattersoni (Gray)	Utah, Colo., Ariz., N. Mex., Tex.
A. pattersoni var. praelongus (Sheld.) (Jones)	Nev., Utah, Ariz., N. Mex.
A. preussii (Gray)	Nev., Utah, Calif., Ariz., N. Mex.
A. recedens (Jones) n. comb.	Colo., N. Mex.
A. sabulosus (Jones)	Utah, Ariz.

Xylorrhiza

Species	Distribution
Xylorrhiza glabriuscula (Nutt.)	Colo., S. Dak., Wyo.
X. parryi (Gray) (Greene)	Wyo.
X. venusta (Jones) (Heller)	Utah, Colo.
X. tortifolius (Gray) (Greene)	Ariz., Calif.
X. villosa (Nutt.)	Colo.

Oonopsis

Species	Distribution
Oonopsis argillacea (A. Nels.)	Wyo., S. Dak.
O. condensata (A. Nels.)	Wyo.

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[9] Modified from Trelease, S. F., and Beath, O. A., (172).

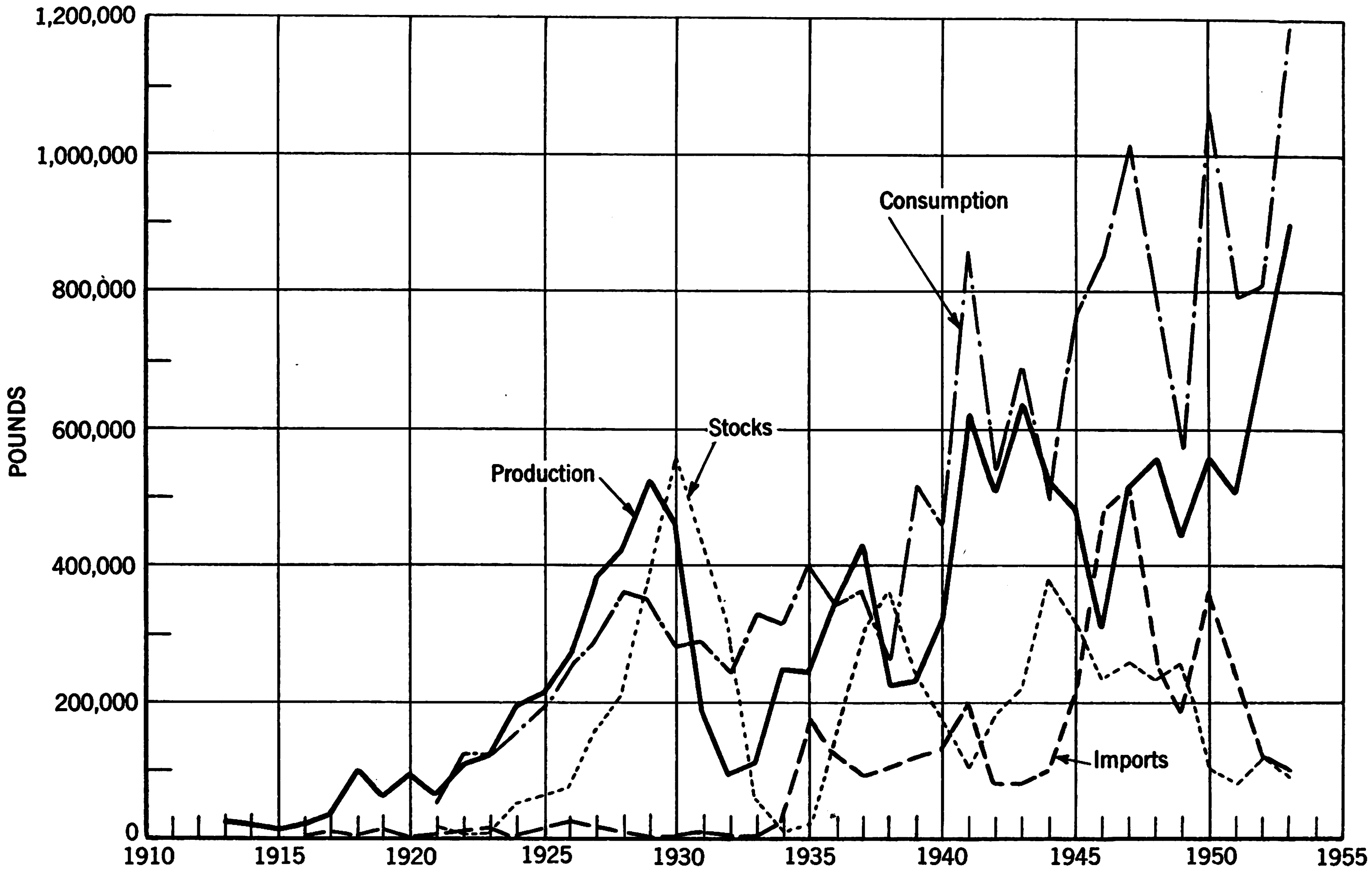

Figure 2. - United States selenium statistics.

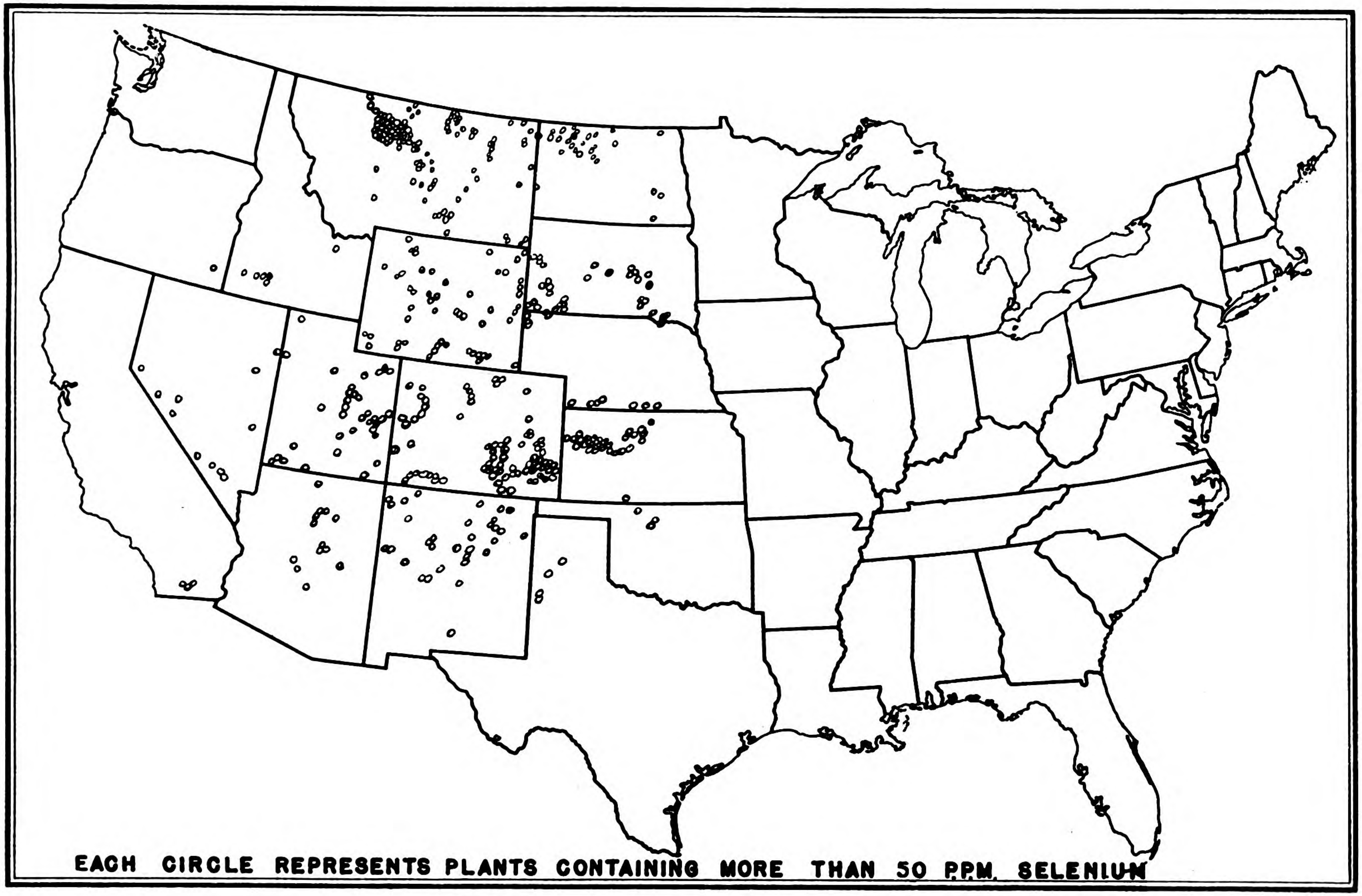
EACH CIRCLE REPRESENTS PLANTS CONTAINING MORE THAN 50 P.P.M. SELENIUM

Figure 3. - Distribution of seleniferous vegetation.

Oonopsis (Con.)

Species	Distribution
O. monocephala (A. Nels)	Colo.
O. engelmannii (Gray) (Greene)	Colo., Kans.
O. foliosa (Gray) (Greene)	Ala.
O. wardii (Gray) (Greene)	Wyo.

Stanleya

Stanleya albescens (Jones)	Colo., Ariz., N. Mex.
S. pinnata (Pursh) (Britt.)	Utah, Wyo., S. Dak., N. Dak., Kans., Ariz., Calif., Colo., Mont., Idaho, Nev., N. Mex., Tex.
S. tomentosa (Parry)	Wyo.
S. vividiflora (Nutt.)	Mont., Ore., Idaho, Wyo., Nev., Utah

Several other species of Xylorrhiza, Oonopsis, and Stanleya may be selenium concentraters as will as some species of Aster, Atriplex, Castilleja, Grayia, Grindelia, Gutierrezia, Ma chaeranthera, Mentzelia, and Sideranthus.

APPENDIX E

Salient statistics of elemental selenium in the United States, 1940-53, in pounds1/
(See fig. 3)

Year	Production2/	Primary producers		Imports3/	
		Domestic shipments	Stocks at end of year	Pounds	Value
1940	328,731	330,207	178,873	134,429	$198,163
1941	620,493	661,171	105,026	197,873	288,161
1942	502,396	442,482	174,803	83,666	127,004
1943	643,660	613,434	225,828	81,720	142,032
1944	525,331	394,818	379,137	97,800	170,582
1945	486,815	554,944	324,967	216,793	395,934
1946	298,233	378,254	232,615	475,881	806,205
1947	511,612	492,716	259,532	529,175	893,175
1948	557,402	527,137	231,294	267,118	489,762
1949	441,898	398,456	265,837	172,636	318,046
1950	558,931	715,185	106,458	363,597	768,544
1951	494,912	547,582	85,123	246,652	1,018,263
1952	687,384	690,978	132,948	4/123,135	564,326
1953	923,887	1,053,236	94,660	99,865	456,663

1/ Bureau of Mines, Minerals Yearbook, 1940 to 1953.
2/ Primary selenium production only, as reported by primary producers.
3/ Includes selenium dioxide and salts.
4/ Includes DDQ grade selenium from Canada under toll arrangement.

BIBLIOGRAPHY

For a comprehensive review and bibliography of the uses of selenium, see Watkins, G. R., Bearse, A. E., and Shutt, R., (176).

A comprehensive review and bibliography of the biology and geology of selenium appears in the book titled Selenium prepared by Trelease, S. F., and Beath, O. A. (172).

A booklet titled Selenium prepared by Paul Tyler (173) gives a comprehensive review of selenium as a metal of strategic importance.

A Bureau of Mines publication by R. M. Santmyers (143) was similar in nature to this paper.

Early publications concerning selenium are listed by M. F. Doty in her selenium bibliography (42).

For an annual accounting of selenium, consult Bureau of Mines Minerals Yearbooks.

Additional selenium references can be obtained from Chemical Abstracts.

1. ALBER, H. K., and HARAND, J. Gravimetric Microdetermination of Selenium in Organic Compounds. Jour. Franklin Inst., vol. 228, 1939, pp. 243-250.

2. AMOR, A. J., and PRINGLE, P. A Review of Selenium as an Industrial Hazard. Bull. Hyd., vol. 20, 1945, pp. 239-241.

3. ANCIZAS-SORDO, J. Occurrence of Selenium in Soils and Plants of Colombia, South America. Soil Sci., vol. 63, 1947, pp. 437-438.

4. AREND, A. G. Selenium Recovery - Its Development in Metallurgical Processes. Chem. Age (London), Jan. 6, 1945, pp. 11-14.

5. BAKER, W. A., and HALLOWES, A. P. C. Experiments on the Removal of Selenium and Tellurium From Blister and Fire-Refined Copper. Bull. Inst. Min. and Met., No. 521, April 1950, pp. 49-50.

6. BARNARD, GEORGE P. The Selenium Cell, Its Properties and Applications. Constable es Co., Ltd., (London,) 1930, 331 pp.

7. BEATH, O. A. Selenium in Native Range Plants Occurring on Soils Derived From Permian and Triassic (?) Sediments. Science, vol. 83, 1936, p. 104.

8. _____. The Occurrence of Selenium and Seleniferous Vegetation in Wyoming. II. Seleniferous Vegetation. Wyoming Agric. Exper. Sta. Bull. No. 221, 1937, pp. 29-64.

9. _____. Toxic Vegetation Growing on the Salt Wash Sandstone Member of the Morrison Formation. Am. Jour. Bot., vol. 30, 1943, pp. 698-707.

10. BEATH, O. A., DRAIZE, J. H., EPPSON, H. F., GILBERT, C. S. and McCREARY, O. C. Certain Poisonous Plants of Wyoming Activated by Selenium and Their Association With Respect to Soil Types. Jour. Am. Pharm. Assoc., vol. 23, 1934, pp. 94-97.

11. BEATH, O. A., DRAIZE, J. H., EPPSON, H. F., GILBERT, C. S. and McCREARY, O.C. Selenium and Other Toxic Minerals in Soils and Vegetation. Wyoming Agric. Exper. Sta. Bull. No. 206, 1935, pp. 1-55.

12. BEATH, O. A., EPSON, H. F., and GILBERT, C. S. Selenium Distribution in and Seasonal Variation of Type Vegetation Occurring on Seleniferous Soils. Jour. Am. Pharm. Assoc., vol. 26, 1937, pp. 394-405.

13. BEATH, O. A., GILBERT, C. S., and EPPSON, H. F. Selenium in Soils and Vegetation Associated With Rocks of Permian and Triassic Age. Am. Jour. Bot., vol. 24, 1937, pp. 96-101.

14. _____. The Use of Indicator Plants in Locating Seleniferous Areas in Western United States. I. General. Am. Jour. Bot., vol. 26, 1939, pp. 257-269.

15. _____. The Use of Indicator Plants in Locating Seleniferous Areas in Western United States. II. Correlation Studies by States. Am. Jour. Bot., vol. 26, pp. 296-315.

16. _____. The Use of Indicator Plants in Locating Seleniferous Areas in Western United States. III, Further Studies. Am. Jour. Bot., vol. 27, 1940, pp. 564-573.

17. _____. The Use of Indicator Plants in Locating Seleniferous Areas in Western United States. IV. Progress report. Am. Jour. Bot., vol. 28, 1941, pp. 887-900.

18. BEATH, O. A., HAGNER, A. F., and GILBERT, C. S. Some Rocks and Soils of High Selenium Content. Wyoming Geol. Survey Bull. 36, 1946, pp. 1-23.

19. BENARD, FREDERICK. Recovery of Selenium at Copper Cliff. Am. Inst. of Min. and Met. Eng., Tech. Paper 908, vol. 5, 1938, pp. 9.

20. BERNHEIM, F., and KLEIN, J. R. Action of Sodium Selenite on the Oxidation of l-Proline. Jour. Biol. Chem., vol. 139, 1941, pp. 827-833.

21. BETTERTON, JESSEE O., and LEBEDEFF, YURII E. Process for Recovering Selenium. (American Smelting & Refining Co.) U. S. Patent 2,378,824, June 19, 1945.

22. BIGELOW, MAURICE HUBBARD and SILVERMAN, ALEXANDER. Selenium Ruby Glass; Preparation and X-ray Study. Jour. Am. Ceram. Soc., vol. 16, 1933, pp. 214-219.

23. BLOCK, M. Selenium Deposit in Pacajahe, Bolivia. Echo des Mine et de la Metallurgic, No. 3287, Sept. 10, 1937, p. 338.

24. BOGGS, C. R., and FOLLANSBEE, E. M. Selenium in Rubber Compounds. Trans. Inst. Rubber Ind., vol. 2, 1926, pp. 272-304.

25. BYERS, H. G. Selenium Occurrence in Certain Soils in the United States, With a Discussion of Related Topics. U. S. Dept. Agric. Tech. Bull. No. 482, 1935, pp. 1-47.

26. _____. Selenium Occurrence in Certain Soils in the United States, With a Discussion of Related Topics: Second Report. U. S. Dept. Agric. Tech. Bull. No. 530, 1936, pp. 1-78.

27. BYERS, H. G., MILLER, J. T., WILLIAMS, K. T., and LAKIN, H. W. Selenium Occurrence in Certain Soils in the United States, With a Discussion of Related Topics: Third Report. U. S. Dept. Agric. Tech. Bull. No. 601, 1938, pp. 1-74.

28. BYERS, H. G., WILLIAMS, K. T., and LAKIN, H. W. Selenium in Hawaii and Its Probable Source in the United States. Ind. and Eng. Chem., vol. 28, 1936, pp. 821-823.

29. CHADWICK, E. W. Voltage Multiplier Circuits With Selenium Rectifiers. Communications, vol. 27, No. 1, January 1947, p. 14.

30. CHEMISTRY AND INDUSTRY. Selenium for Electrical Industry. London, No. 31, Aug. 1, 1953, p. 808.

31. CHIHAYA, TADASHI, SHIOTA, NOBUO, AND ONOSAKI, CHOEI. [Fundamental Studies on Selenium. II.] Nippon Kinzoku Gakkai-Shi (Ibaragi Univ.), Bull. 14, 1950, pp. 43-45.

32. CLARK, C. W., and SCHLOEN, J. H. Production of Selenium at Montreal East. Am. Inst. of Min. and Met. Eng., Tech. Paper 982, vol. 5, 1938, 22 pp.

33. _____. Production of Selenium at Montreal East. Am. Am. Inst. of Min. and Met. Eng., Trans., vol. 159, 1944, pp. 495-520.

34. CLINTON, JR., M. Selenium Fume Exposure. Jour. Ind. Hyg. Toxicol., vol. 29, 1947, pp. 225-226.

35. CULLITY, B. R., TELKES, M., and NORTON, JOHN T. Electrical Resistivity and Thermoelectric Power of Antimony-Selenium Alloys. Trans. Am. Inst. Min. and Met. Eng., Jour. Metals, vol. 188, No. 1, Jan. 1950, pp. 47-52.

36. CURL, A. L., and OSBORN, R. A. Report on Selenium. Jour. Assoc. Official Agr. Chem., vol. 21, 1938, pp. 228-235.

37. D'ALBE, E. E., FOURNIER, and SYMONDS, B. A. Some New Applications of Selenium. Proc. of the Optical Conv., 1926, p. 884.

38. DAVIDSON, W. B. Selenium Poisoning. Canadian Jour. Comp. Med., vol. 4, 1940, pp. 19-25.

39. DAY, F., JR., and SILVERMAN, A. Oxidation - Reduction Equilibria in Glass Between Iron and Selenium in Several Furnace Atmospheres. Jour. Am. Ceram. Soc., vol. 25, No. 13, 1942, pp. 371-381.

40. DIETZEL, A. The Theory of Declorizing With Selenium. Jour. Soc. Glass Tech., vol. 21, 1937, pp. 87-94.

41. DOLIQUE, R. and GIROUX, J. The Fate of Selenium After Poisoning by Sodium Selenite and Selenate. Soc. chim., Bull. 10, 1943, pp. 60-64.

42. DOTY, M. F. Selenium Bibliography, 1817-1925. New York Public Library, New York, 1926, 114 pp.

43. DOWNIE, C.C. Metallurgical Fume and Flue Dusts. Min. Mag., vol. 86, No. 2, February 1952, pp. 80-83.

44. DUDLEY, H. C. Selenium as a Potential Industrial Hazard. Pub. Health Rept., vol. 53, 1938, pp. 281-292.

45. _____. Toxicology of Selenium. I. A Study of the Distribution of Selenium in Acute and Chronic Cases of Selenium Poisoning. Am. Jour. Hyg., vol. 23, 1936, pp. 169-180.

46. _____. Toxicology of Selenium. II. The Urinary Excretion of Selenium. Am. Jour. Hyg., vol. 23, 1936, pp. 181-186.

47. _____. Toxicology of Selenium. III. Determination of Selenium in Air-Gas-Dust Mixtures. Am. Jour. Hyg., vol. 24, 1936, pp. 227-236.

48. _____. Toxicology of Selenium. V. Toxic and Visicant Properties of Selenium Oxychloride. Pub. Health Rept., vol. 53, 1938, pp. 94-98.

49. DUDLEY, H. C., and BYERS, H. G. Determination of Selenium; Quantitative Determination on Animal Matter and Clinical Test in Urine. Ind. Eng. Chem., vol. 7, 1935, pp. 3 - 4.

50. DUDLEY, H. C., and MILLER, J. W. Toxicology of Selenium. IV. Effects of Exposure to Hydrogen Selenide. Pub. Health Rept., vol. 52, 1937, pp. 1217-1231.

51. _____. Toxicology of Selenium. VI. Effect of Subacute Exposure to Hydrogen Selenide. Jour. Ind. Hyg. and Toxicol., vol. 23, 1941, pp. 470-477.

52. DUNOYER, JEAN M. /A Transformation of Selenium at Low Temperature./ Compt. rend., vol. 226, 1948, pp. 1524-1525.

53. DYSON, G. M. The Extraction and Uses of Selenium. (Monthly Met. Sect.) Chem. Age (London), vol. 18, No. 453, 1928, pp. 17-19.

54. EDGINGTON, GLEN, and BEYERS, H. G. Geology and Biology of North Atlantic Deep Sea Cores. Geol. Survey Prof. Paper 196-F, part 9, 1942, pp. 151-155.

55. ELLIS, M. M., MOTLEY, H. L., ELLIS, M. D., and JONES, R. O. Selenium Poisoning in Fishes. Proc. Soc. Expe. Biol. and Med., vol. 36, 1937, pp. 519-522.

56. ENGINEERING AND MINING JOURNAL. Uses of Selenium in the Rubber Industry. Vol. 123, Apr. 30, 1927, p. 734.

57. FALCIOLA, P. /New Researches on Selenium and Tellurium./ Ann. chim. appl., vol. 17, 1928, p. 357.

58. FALL, HARRY H. Selenium Dehydrogenation of Cholesterol, Cholestane and Optically Active Petroleum Fractions. Thesis - Pennsylvania State College. Ann Arbor, Mich., University Microfilms, 1950.

59. FIELDING, T. J. Photoelectric and Selenium Cells; Their Operation, Construction and Uses. Chapman & Hall, Ltd. (London), 1935, 140 pp.

60. FITZHUGH, O. G., NELSON, A. A., and BLISS, C. I. Chronic Oral Toxicity of Selenium. Jour. Pharmacol. Exp. Therap., vol. 80, 1944, pp. 289-299.

61. FOURNIER, HENRI. /Protection of Magnesium by Means of Selenium-Coatings./ Metaux, vol. 9, 1934, pp. 506-508.

Digitized by Google Original from THE OHIO STATE UNIVERSITY

62. FRANKE, K. W., and PAINTER, E. P. Effect of Sulfur Additions on Seleniferous Soils. Binding of Selenium by Soil. Ind. Eng. Chem., vol. 29, 1937, pp. 591-595.

63. GAEV, A. I., and BEZDENEZHNIKH, A. C. [Production of Selenium in the Uran Electrolytic Plants.] Tsvetnye Metal., No. 5, 1938, pp. 50-57.

64. GAGNEBIN, ALBERT P. Selenium Additions to Cast Steel. Am. Foundryman, vol. 12, August 1947, pp. 43-52.

65. GNADINGER, C. B. Selenium. Insecticide Material for Controlling Red Spider. Ind. Eng. Chem., vol. 25, 1933, pp. 633-637.

66. GOLDSCHMIDT, V. M., and STROCK, L. W. [The Geochemistry of Selenium. II.] Nachr. Ges. Wiss. Gottingen, Math.-Phys. Kl., vol. 1, 1935, pp. 123-142.

67. GRISON, E. Tellurium-Selenium Alloys. Jour. Chem. Phys., vol. 19, 1951, pp. 1109-1113.

68. HAMILTON, A. Industrial Toxicology. Harper & Bros., New York, N. Y., 1934, 352 pp.

69. HANSON, ROBERT LEWIS. The Photo-emf in Selenium. Jour. Opt. Soc. America, vol. 18, 1929, pp. 370-382.

70. HARLOFF, C. S., and JOHNSON, H. F. The Nichols Series System of Electrolytic Copper Refining. Am. Inst. of Min. and Met. Eng., vol. 106, 1933, p. 403.

71. HEIKS, RAY E., and CROXTON, FRANK C. Selenium Dioxide as a Lubricant Additive. Ind. Eng. Chem., vol. 39, No. 11, November 1947, pp. 1466-1474.

72. HENKELS, HERBERT W. Properties of Single-Crystal Selenium Prepared From a Melt. Phys. Rev., vol. 76, 1949, pp. 1737-1738.

73. _____. Electrical Properties of Selenium, Part I. Jour. Applied Phys., vol. 22, 1951, pp. 916-925; Part II. pp. 1265-1278.

74. HOFFMAN, G. F., and LENHER, VICTOR. Precipitated Selenium Dioxide. Jour. Am. Chem. Soc., vol. 51, 1929, pp. 3177-3184.

75. HOFLER, W., and A. DIETZEL. [The Tempering of Selenium Iron Glasses and Its Significance for the Process of Decolorizing With Selenium.] Glastech. Ber., vol. 14, 1936, pp. 411-421.

76. HOFLER, WOLFGANG. [The Behavior of Selenium in Glasses.] Glastech Ber. 12, vol. 12, 1934, pp. 117-134.

77. HOSKINS, W. M., BOYCE, A. M., and LAMIMAN, J. F. The Use of Selenium in Sprays for the Control of Mites on Citrus and Grapes. Hilgardia, vol. 12, 1938, pp. 115-175.

78. HUKKI, R. T. and RUNOLINNA, U. Separation of Precious Metals From Anode Slimes by Flotation. Trans. Am. Inst. Min. and Met. Eng., vol. 187, November 1950, p. 1131.

79. HURD-KARRER, (Mrs.) ANNIE MAY. Selenium Absorption by Plants and Their Resulting Toxicity to Animals. Smithsonian Institution Annual Report, 1935., pp. 289-301

80. INDIA RUBBER WORLD. Selenium and "Vandex". A Description of the Properties and Uses of the New Commercial Product "Vandex." Vol. 76, 1927, p. 136.

81. IRON AGE. Selenium. Vol. 170, No. 14, Oct. 9, 1952, pp. 283-284.

82. JULEK, A. and LUKAS, A. Electrodeposition of Selenium. Chemistry, vol. 21, 1927, p. 576.

83. KAPLAN, HARRY. The Use of Selenium Dioxide in the Preparation of Quinoline Aldehydes and Condensation Reactions of Cinchoninaldehyde and Quinaldealdehyde. Jour. Am. Chem. Soc., vol. 63, No. 10, October 6, 1941, pp. 2654-2655; vol. 65, No. 15, May 12, 1943, pp. 927-928.

84. KAZANTSEV. A. [Direct Extraction of Selenium From Sulfuric Acid Sludge.] Novosti Tekhniki, vol. 10, No. 5, 1941, pp. 36-37. Chem. Zentr., alb., vol. I, 1942, pp. 2050-2051.

85. KECK, PAUL H. The Electrical Properties of Selenium Coatings. Jour. Opt. Soc. America, vol. 41, 1951, pp. 53-55.

86. KIPLINGER, D. C., and FULLER, G. Selenium Studies With Some Flowering Greenhouse Plants. Proc. Am. Soc. Hort. Sci., vol. 47, 1946, pp. 451-462.

87. KLEIN, A. K. Report on Selenium. Jour. Assoc. Official Agric. Chem., vol. 24, 1941, pp. 363-380; vol. 25, 1942, pp. 403-410; vol. 26, 1943, pp. 346-352.

88. KNIGHT, S. H. Occurrence of Selenium and Seleniferous Vegetation in Wyoming. Wyoming Agric. Exper. Station, Bull. No. 221, 1937, pp. 3-64.

89. KRAK, J. B. Selenium in Ruby Glass. Foote Prints, vol. 2, No. 1, 1929, p. 30.

90. KREBS, H. [Black Selenium. IV. The Structure of Glassy Selenium and Its Catalytic Conversion to the Hexagonal Crystalline Form.] Ztschr. anorg. allgem. chem., vol. 265, 1951, pp. 156-168.

91. KREBS, H. and MORSCH, W. [Black Selenium. III. The Molecular Weight of Amorphous Black Selenium.] Ztschr. anorg. allgem. chem., vol. 263, 1950, pp. 305-309.

92. LAKIN, H. W. and BYERS, H. G. Selenium Occurrence in Certain Soils in the United States, With a Discussion of Related Topics: Sixth Rept. U. S. Dept. Agric. Tech. Bull. 783, 1941, pp. 1-26.

93. _____. Selenium Occurrence in Certain Soils in the United States, With a Discussion of Related Topics: Seventh Report. U. S. Dept. Agric. Tech. Bull. No. 950, 1948, pp. 1-36.

94. LE BROCQ, L. F., and COLE, H. G. Selenium Coatings for the Protection of Magnesium Alloys Against Corrosion. Selected Govt. Res. Repts., (London), Protection and Electro-Deposition of Metals, vol. 3, 1951, pp. 259-266. vol. 3, 1951, pp. 259-266.

95. LEMLEY, R. E. Selenium Poisoning in the Human. Jour. Lancet, vol. 60, 1940, pp. 528-531.

96. LEMLEY, R. E., and MERRYMAN, M. P. Selenium Poisoning in the Human. Jour. Lancet, vol. 61, 1941, pp. 435-438.

97. LENHER, V. The Quantitative Determinations of Selenium and Tellurium. Proc. Am. Phil. Soc., vol. 65, 1927, pp. 38-50.

98. LENHER, VICTOR, and FRUEHAN, A. G. Seleno Compounds of Tungsten. Jour. Am. Chem. Soc., vol. 49, 1927, pp. 3076-3080.

99. LINDBLAD, AXEL R. [Selenium.] German Patent 641714, Feb. 11, 1937.

100. _____. [Recovery of Selenium in Copper Refining.] Swedish Patent 84,053, Aug. 13, 1935.

101. LITTMAN, Z. [Selenium Recovery From Lead-Chamber Sludge.] Chem.-Ztg., vol. 50, 1926, p. 704.

102. LIZELL, B. The Electrical Conductivity of Liquid Selenium and Selenium-Tellurium Mixtures. E Laboratory for Insulation Research, Mass. Inst. of Tech. Submitted in partial fulfillment of the requirements for the degree of Master of Science, September 1951, 38 pp.

103. MANNING, W. H. Are You Saving Enough Selenium? Ceram. Ind., vol. 59, No. 6, December 1952, pp. 84-85.

104. MANVILLE, I. A. The Selenium Problem and Its Relationship to Public Health. Am. Jour. Pub. Health, vol. 29, 1939, pp. 709-719.

105. MARTIN, A. L. Toxicity of Selenium to Plants and Animals. Am. Jour. Bot., vol. 23, 1936, pp. 471-483.

106. MARTIN, DONALD CLAYTON. Analysis of the Spectrum of Selenium II. Lancaster Press, Inc., Lancaster, Pa., 1935.

107. MARTIN, OLIVER C., and CLARK, CHARLES W. Recovery of Selenium and Tellurium From Slimes. United States Patent 2,039,256, pr. 28, 1936.

108. MATHEWS, J. A., CURL, A. L., and OSBORN, R. A. Report on Selenium. Jour. Assoc. Official Chem., vol. 20, 1927, pp. 194-202.

109. METAL INDUSTRY. Selenium and Its Potentialities. Vol. 33, No. 3, July 20, 1928, p. 66.

110. METAL INDUSTRY (London). Selenium, Notes on Use and Properties of Selenium. Vol. 30, 1927, p. 30.

111. MEYER, H. C., Selenium and Tellurium. Eng. and Min. Jour., vol. 123, 1927, p. 136.

112. _____. Uncommon Ores and Metals: Review of Selenium and Tellurium for the Year 1927. Eng. and Min. Jour., vol. 125, 1928, p. 96.

113. MEYER, J. and PAWLETTA, A. [The Preparation of Selenium Trioxide.] Ber. deut. chem. Gesell., vol. 60 B, 1927, p. 985.

114. MORINAGA, TAKUICHI: CHIHAYA, TADSHI: SHIOTA, NOBUO; and ONOZAKI, CHOEI. [Selenium.] Nippon Kinzoku Gakkai-si, Jour. Japan Inst. Metals, vol. 14B, No. 3, 1950, pp. 40-41.

115. MOSHER, M. A. Recovery of Precious and Secondary Metals From Electrolytic Copper Refining. Trans. Am. Inst. of Min. and Met. Eng., vol. 106 (Copper Metallurgy), 1933, pp. 427-440.

116. MOSHKOVICH, S. M. [Selenium Light-Sensitive Cell.] Russian Patent 5295, May 31, 1928; Chem. Abs., vol. 23, May 10, 1929, p. 2076.

117. MOXON, A. L., and OLSON, O. E. Selenium Content of Plants and Soils. South Dakota Agric. Exper. Sta. 53rd Ann. Rept., 1940, p. 15.

118. MOXON, A. L., and RHIAN, M. Selenium Poisoning. Phys. Rev., vol. 23, 1943, pp. 305-337.

119. MOXON, A. L., OLSON, O. E., and SEABRIGHT, W. V. Selenium in Rocks, Soils, and Plants. South Dakota Agric. Exper. Station Tech. Bull. 2, 1939, pp. 1-94.

120. MOXON, A. L., OLSON, O. E., SEABRIGHT, W. V., and SANDALS, K. M. The Stratigraphic Distribution of Selenium in the Cretaceous Formations of South Dakota and the Selenium Content of Some Associated Vegetation. Am. Jour. Bot., vol. 25, 1938, pp. 794-809.

121. MURPHY, JOHN, and LOCKEWWITZ, ARTHUR E. The Time Rate of Transformation of Monoclinic Selenium Into Hexagonal as a Function of Temperature. Phys. Rev., vol. 85, pp. 745-746.

122. NASLEDOV, D. N., and MALYSHEV, E. K. [Electric Conductivity of Amorphous Selenium.]

123. _____. [Polarization Phenomena in Amorphous Selenium. Jour. Tech. Phys.] (U.S.S.R.) (in Russian), vol. 16, 1946, pp. 1135-1140.

124. NATURE. Photography on Selenium. Vol. 161, Apr. 3, 1948, p. 522.

125. NELSON, E. M., HURD-KARRER, A. M., and ROBINSON, W. O. Selenium as an Insecticide. Science, vol. 78, 1933, p. 124.

126. NEUMANN, KURT, and LICHTENBERG, ERNST. [Molecular-Weight Determination and the Vapor Pressure of Selenium.] Ztscher. physick. Chem., vol. A184, 1939, pp. 89-99.

127. NOYES, A. A., and BRAY, W. C. A System of Qualitative Analysis for the Rare Elements. The MacMillan Co., New York, 1927, 536 pp.

128. NUMATA, TADASI. [Electric Properties of Selenium-Tin Alloy.] Kyushu Univ., Fukuoka, Busseiron Kenkyu, Researches on Chem. Phys., No. 27, 1950, pp. 1-10.

129. PAVLISH, A. E., and AUSTIN, C. R. Selenium-Ruby and Other Glasses Colored by Selenium. Jour. Am. Ceram. Soc., vol. 30, No. 1, Jan. 1, 1947, pp. 1-11.

130. PENIN, N. A., and ASTAKHOV, K. V. [Effect of Admixtures to Selenium on the Electric Properties of Selenium Rectifiers.] Jour. Tech. Phys. (U.S.S.R.), vol. 16, 1946, pp. 199-206.

131. PHILLIPS, ALBERT J., LEBEDEFF, YURII, E., and CRANDALL, JAMES R. Recovery of Elemental Selenium. United States Patent 2,413,374, Dec. 31, 1946.

132. PLESSNER, K. W. Conductivity and Hall Effect of Microcrystalline Selenium Containing Iodine Impurities. Proc. Phys. Soc. (London), vol. 64B, 1951, pp. 681-690.

133. _____. Conductivity, Hall Effect, and Thermoelectric Power of Selenium Single Crystals. Proc. Phys. Soc. (London), vol. 64B 1951, pp. 671-681.

134. POLAND, F. F., to American Smelting & Refining Co. Recovery of Selenium. United States Patent 2,048,563, July 21, 1936.

135. PRINGLE, P. Occupational Dermatitis Following Exposure to Inorganic Selenium Compounds. Brit. Jour. Dermatol. Syphilis, vol. 54, 1942, pp. 54-58.

136. RADER, L. F., Jr., and HILL, W. L. Occurrence of Selenium in Natural Phosphates, Superphosphates, and Phosphoric Acid. Jour. Agric. Res., vol. 51, 1935, pp. 1071-1083.

137. RALSTON, OLIVER, C., and KLEIN, LEONARD, to United Verde Copper Co. Selenium Recovery From Copper Sulfide Ores. United States Patent 1,945,074, Jan. 30, 1934.

138. RANKAMA, K., and SAHAMA, T. G. Geochemistry. Univ. of Chicago Press, 1949, 911pp. pp.

139. RANKINE, A. O., and AVERY, J. W. Electrical Polarization of Selenium Cells. Proc. Phys. Soc. (London), vol. 39, 1927, p. 187.

140. _____. The Sensitivity of Selenium Cells. Nature, vol. 118, July 13, 1926, p. 13.

141. ROBINSON, W. O., DUDLEY, H. C., WILLIAMS, K. T., and Byers, H. G. Determination of Selenium and Arsenic by Distillation. Ind. Eng. Chem., vol. 6, 1934, pp. 274-276.

142. SAKER, E. W. The Optical Properties of Liquid Selenium. Proc. Phys. Soc. (London), vol. 65B, 1952, pp. 785-787.

143. SANTMYERS, R. M. Selenium and Tellurium. Bureau of Mines Inf. Circ. 6317, 1930, pp. 1-15, 21, 22.

144. SATO, TOMO-O, and KENEKO, HIDEO. [Selenium and Its Alloys. IV. Effect of Additional Elements on Electrical Resistance of Selenium.] Nippon Kinzoku Gakkai-si, Jour. Inst. Metals, vol. 14B, No. 3, 1950, pp. 33-35.

145. _____. [Studies on Selenium and Its Alloys. II. Some Experiments on the Rectifying Characteristics of Selenium Rectifier.] Tech. Repts., Tohoku Univ., vol. 15, 1950, pp. 1-10.

146. _____. [Selenium and Its Alloys. III. Vapor Pressure and Electric Conductivity of Molten Selenium Alloys.] Technol. Repts. Tohoku Univ., vol. 16, No. 2, 1952, pp. 18-33.

147. SCHLOEN, J. H., and ELKIN, E. M. Canadian Copper Refiners Montreal East Plant. Canadian Min. and Met. Bull. 408, April 1946, pp. 185-188.

148. _____. Treatment of Electrolytic Copper Refinery Slimes. Jour. Metals, vol. 188, 1950, pp. 764-777.

149. SEABRIGHT, W. V., and MOXON, A. L. Selenium in Glacial and Associated Deposits. South Dakota Agric. Exper. Station Tech. Bull. vol. 5, 1945, pp. 1-33.

150. SEABRIGHT, W. V., MOXON, A. L., WHITEHEAD, E. I., and VIETS, F. G., Jr. Detailed Mapping of Seleniferous Vegetation on Soils of Pierre Origin. South Dakota Acad. Sci., Proc., vol. 26, 1946-1947, pp. 87-98.

151. SHAW, EDWIN HERBERT. Some Derivatives of Ethyl Selenomercaptan and a New Method for the Quantitative Estimation of Selenium in Organic Compouuds. Mack Printing Co., Easton, Pa., 1926.

152. SILVERTHORN, R. W. Analysis of Compounds Containing Selenium. Chem. Analyst., vol. 30, 1941, pp. 52-54, 62,63.

153. SMITH, ARTHUR L., and OTHERS. Preparation of Strontium Selenide and Its Properties as a Base Material for Phosphors Stimulated by Infrared. Jour. Am. Chem. Soc., vol. 69, No. 7, July 1947, pp. 1725-1729.

154. SMITH, CYRIL STANLEY. Sulphur, Selenium and Tellurium in Copper-Base Alloys. Metals Technol., vol. 24, No. 8, 1937, 10 pp.

155. SMITH, MAURICE ISADORE. Chronic Endemic Selenium Poisoning. Jour. Am. Med. Assoc., vol. 116, 1941, pp. 562-566.

156. _____. The Selenium Problem in Relation to Public Health. A Preliminary Survey to Determine the Possibility of Selenium Intoxication in the Rural Population Living on Seleniferous Soil. Govt. Printing Office, Washington, D. C. 1936.

157. _____. Studies on the Fate of Selenium in the Organism. Div. of Pharmacology, Nat. Inst. of Health, U. S. Public Health Service. U. S. Govt. Printing Office, Washington, D. C., 1938.

158. _____. Studies in Chromic Selenosis. Div. of Pharamocology, Nat. Inst. of Health, U. S. Public Health Service. U. S. Govt. Printing Office, Washington, D. C., 1940.

159. _____. Further Field Studies on the Selenium Problem in Relation to Public Health. Div. of Pharmacology, Nat. Inst. of Health, U. S. Govt. Printing Office, Washington, D. C., 1937.

160. _____. The Elimination of Selenium and Its Distribution in the Tissues. Div. of Pharmacology, Nat. Inst. of Health, U. S. Public Health Service. U. S. Govt. Printing Office, Washington, D. C., 1937.

161. SMITH, M. I., STOHLMAN, E. F., and LILLIE, R. D. The Toxicity and Pathology of Selenium. Jour. Pharmacol. and Exp. Therap., vol. 60, 1937, pp. 449-471.

162. SPRINGER, L. Melting Investigation Pertaining to the Coloring of Glass. Sprechsaal, vol. 59, 1926, p. 530.

163. STAHL, W. [Selenium Recovery From Lead Chamber Slimes.] Chem. Ztg., vol. 50, 1926, p. 280.

164. STEIGMAN, A. More about Gold-Selenium Toning. Camera (Luzern), vol. 4, 1926, p. 208.

165. STOVER, NORMAN McKEE, and HOPKINS, B. S. Fungicidal and Bactericidal Action of Selenium and Tellurium Compounds. Ind. Eng. Chem. vol. 19, 1927, pp. 510-513.

166. STORCK, L. W. The Distribution of Selenium in Nature. Am. Jour. Pharm., vol. 107, 1935, pp. 144-157.

167. SULLIVAN, W. P. Preventing a Shrinkage in Gray Iron Castings; Tellurium Core Washes as Chill Inducers. Am. Foundryman, vol. 12, August 1947, pp. 26-28.

168. TAKEI, TAKESHI, AOYAMA, KOZO, and OKADA HIROSHI. Purification of Selenium. Repts. Sci. Res. Inst., vol. 26, 1950, pp. 234-239.

169. TERASAKI, YUTAKA, and SASAKAWA, SHIRO, to Nippon Mining Co. [A New Treatment for Recovering Selenium, Tellurium, Antimony, etc., From Sludge Obtained by the Electrolysis of Copper.] Japanese Patent 2560, July 9, 1952.

170. THORNE, B. T. The Resistivity of Selenium Cells. Nature, vol. 117, 1926, pp. 858-859.

171. TRELEASE, S. F. Selenium in Soils, Plants, and Animals. Soil Sci., vol. 60, 1945, pp. 125-131.

172. TRELEASE, S. F., and BEATH, O. A. Selenium. Columbia Univ. Press, New York, 1949, 292 pp.

173. TYLER, PAUL M. Selenium. Minerals and Metals Advisory Board, Nat. Research Council, Rept. MMAB-15-M, 1952, 62 pp.

174. UETA, RYUZO; TOKIWA, TAKAMICHI; and IKEDA, YOSHIO. [Electrical Conductivity and Thermo-electromotive Force of Single Crystal of Selenium.] Busseiron Kenkyu (Waseda Univ., Tokyo), No. 31, 1950, pp. 85-89.

175. VON HIPPEL, A., and BLOOM, M. C. The Electroplating of Metallic Selenium. M.I.T. Lab. for Insulation Res., Tech. Rept. 34, 1950, 28 pp.

176. WATKINS, G. R., BEARSE, A. E., and SHUTT, R. Industrial Utilization of Selenium and Tellurium. Ind. and Eng. Chem. vol. 34, 1942, pp. 899-910.

177. WALKER, O. J., HARRIS, W. E., and ROSSI, M. Selenium in Soils, Grains, and Plants in Alberta. Canadian Jour. Res., vol. 19, 1941, pp. 173-178.

178. WERNIMONT, G., and HOPKINSON, F. J. Microtitration of Selenium. Ind. Eng. Chem., vol. 12, 1940, pp. 308-310.

179. WILCOX, R. J. Improving Stainless Quality by the Use of Minor Selenium Additions. Alloy Casting Bull. 15, March 1951, p. 1.

180. WILLIAMS, K. T., and BYERS, H. G. Occurrence of Selenium in Pyrites. Ind. Eng. Chem., vol. 6, 1934, pp. 296,297.

181. _____. Occurrence of Selenium in the Colorado River and Some of Its Tributaries. Ind. Eng. Chem., vol. 7, 1935, pp. 431, 432.

182. _____. Selenium in Deep Sea Deposits. Ind. Eng. Chem., vol. 13, 1935, p. 353.

183. WILLIAMS, K. T., and LAKIN, H. W. Determination of Selenium in Organic Matter. Ind. Eng. Chem., vol. 7, 1935, p. 409.

184. WILLIAMS, K. T., LAKIN, H. W., and BYERS, H. G. Selenium Occurrence in Certain Soils in the United States, With a Discussion of Related Topics: Fourth Report. U. S. Dept. Agric. Tech. Bull. No. 702, 1940, pp. 1-59.

185. _____. Selenium Occurrence in Certain Soils in the United States, With a Discussion of Related Topics: Fifth Report. U. S. Dept. Agric. Tech. Bull. No. 758, 1941, pp. 1-69.

186. ZACHIMMER, F. The Question of the Decolorization and Discoloring of Glass. Sprechsaal, vol. 59, 1926, p. 93.

187. ZHURAVELVA, M. G., and CHUFAROV, G. I. [Separation of Sulfur and Selenium.] Shur. Priklad, Khim., vol. 24, 1951, pp. 28-31.